

## Different quantum behavior of the $E_1$ and $E_2$ spectral structures in Ge nanocrystals

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In this paper we report absorption measurements in the range 0.6–6.0 eV, performed at 77 K on Ge nanocrystals grown by a self-organization process applied to a semiconductor. Evidence of a relevant blueshift of  $E_2$  and weakening of  $E_1$  with size reduction is obtained. This behavior is interpreted in terms of quantum confinement in connection with the different nature of the two structures.

The physics of quantum dots presents particularly interesting aspects, mainly related to the strong modifications of the fundamental properties of the material, due to space confinement in three dimensions:<sup>1</sup> remarkable effects on the joint density of states,<sup>2</sup> optical absorption and photoluminescence spectra,<sup>3–8</sup> nonlinear behavior,<sup>9</sup> have been either predicted or observed. Until now, the efforts have been concentrated mainly on the III-V and II-VI semiconductor quantum dots;<sup>3,4,7,9–12</sup> the main reason is related to the fact that the direct gap allows the observation and measurement of relevant signals, with evidence of blueshift of the energy gap with size reduction.

Less literature is presently available on Ge and Si quantum dots, except for absorption and photoluminescence measurements around the band gap<sup>6,8</sup> or specific developments concerning photoluminescence in Si clusters<sup>5</sup> and, finally, the theoretical work recently published by Wang and Zunger.<sup>13</sup>

Here we report absorption measurements above the indirect gap of Ge; for the first time, to our knowledge, a comparative study is performed of the size dependence of the  $E_1$  and  $E_2$  spectral structures in quantum dots with average diameter  $\langle d \rangle$  in the range 25–130 Å. Experimental evidence is obtained of the different behavior of  $E_1$  with respect to  $E_2$ ; the interpretation is given in terms of the specific nature of the two structures.

The samples were prepared by means of evaporation-condensation in UHV on suitable substrates. After evaporation of a film of  $\text{Al}_2\text{O}_3$  (having a thickness of  $\approx 50$  Å) on sapphire, Ge was deposited on top in such a way that its vapor is condensed on alumina. Essential characteristics of the technique are the amorphous nature of  $\text{Al}_2\text{O}_3$ , its nonwetting or partially wetting character with respect to the deposit<sup>14</sup> (Ge in this case, or, also, metals previously grown and studied<sup>15,16</sup>) and the absence of strong perturbations due to chemical etching or mechanical distortions. During evaporation, the temperature of the substrate is kept at such a value that nucleation of Ge takes place in the liquid phase. A self-

organization process leads to a distribution of liquid Ge nanodroplets (all the deposited Ge gives origin to quantum dots). After freezing, an additional layer of alumina can be evaporated to cover and protect the distribution of nanoparticles, so that size and shape are kept constant.

The size distribution is bimodal (presenting an interesting similarity with other techniques<sup>7,17</sup>); its larger portion ( $\approx 95\%$  in volume) is characterized by a relatively low size dispersion ( $\sigma/R \approx 20\%$ , where  $R$  is the average radius). The nanoparticles exhibit the shape of truncated spheres and are single crystals. The obtainable size range is quite wide, typically from ten to a few thousand Å. In order to improve the signal-to-noise ratio in the optical measurements, the total quantity of Ge has been increased by replicating five times the  $\text{Al}_2\text{O}_3/\text{Ge}$  two-layer system; the parameter used to indicate the Ge quantity in each double layer is the so-called equivalent thickness  $t$ , i.e., the thickness of the semiconductor film containing the same volume of material (see Table I for the specific characteristics of the samples).

The crystalline nature of the quantum dots in the whole size range investigated has been verified by means of high-resolution electron microscopy (Fig. 1). Only below  $\langle d \rangle \approx 15$  Å does the growth process become more complex and deserve further analysis, which, however, is not the object of the present work.

The fabrication technique by self-organization can be compared with other procedures based on the two-dimensional–three-dimensional transition of an epitaxial mismatched layer,<sup>7,17</sup> from which an arraylike distribution can be obtained. The technique here adopted appears to open relevant possibilities concerning preparation of particles with a rather regular shape and size which can be varied in a wide range.

The absorption spectra have been collected in a temperature range between 77 and 300 K, using a spectrophotometer Varian Cary 5, in the energy range between 0.6 and 6.0 eV, with a measurement accuracy better than 0.01 eV.

TABLE I. Structural data of the samples investigated ( $t$ : equivalent thickness of the Ge layer in Å;  $\langle d \rangle$  and  $R$ : nanoparticles, average diameter and radius in Å).

Sample	$t$ (single layer)	$\langle d \rangle$ ( $\sigma/R \approx 20\%$ )
1	12	25
2	15	30
3	35	100
4	50	125

In Fig. 2 the curves showing optical absorption versus energy in samples characterized by different values of  $R$  are reported. It is important to clarify that the absorption plotted in the figure is actually obtained by normalizing the recorded experimental curves to the Ge volume, given in each case by the global equivalent layer.<sup>18</sup> In the inset we show the absorption of bulk Ge calculated by the extended  $\mathbf{k} \cdot \mathbf{p}$  theory.<sup>19</sup> From the inspection of Fig. 2 one can notice clear modifications with size of  $E_1$  and  $E_2$ .

$E_2$  is first considered, due to its nature as more directly amenable to contributions of specific points in the Brillouin zone (BZ) [it originates from different portions of the BZ, but the peak structure comes essentially from the Chadi-Cohen special point, i.e.,  $(\frac{3}{4}, \frac{1}{4}, \frac{1}{4})$ <sup>19,20</sup>]. In Fig. 3 the shift of  $E_2$  versus size is reported, with a maximum displacement of 0.14 eV in the nanocrystals having a mean diameter of about 25 Å with respect to the sample containing the bigger particles ( $\langle d \rangle \approx 130$  Å).

Although a blueshift of spectral structures is generally observed in confined systems, here the interpretation is not as simple as it is in the case of effective-mass-like critical points, since the spectral strength of the  $E_2$  transition comes from  $\mathbf{k}$  points in the whole Brillouin zone:<sup>19</sup> a confinement-induced blueshift of the  $E_2$  transition can be expected, but a quantitative explanation goes beyond simple effective-mass models. As calculated by Wang and Zunger<sup>13</sup> for Si quantum dots, the confinement shift of the spectral structure does not necessarily grow as  $1/R^2$ , but, in any case, it increases faster than the electron-hole Coulomb attraction, which goes like  $1/R$ ,<sup>10</sup> so that the excitonic enhancement of absorption is expected to be less important in the quantum dots compared to the bulk. Thus an interpretation of the behavior of  $E_2$  versus size can be given considering band-to-band transitions only. The observed blueshift of the  $E_2$  transition is then in line with the theoretical results of Ref. 13 for Si quantum dots; a quantitative interpretation requires theoretical calculations accounting for confinement effects in the whole Brillouin zone.

The different behavior of  $E_1$  with respect to  $E_2$  is illustrated in Fig. 4. The area under peak versus size is reported for the two structures. A strong decrease is observed for  $E_1$  when  $\langle d \rangle \approx 25$  Å, whereas one can notice that the  $E_2$  peak grows when the average radius decreases.

In bulk Ge, the  $E_1$  spectral structure originates from transitions in a large portion of the  $\Gamma$ - $L$  direction in the Brillouin zone.<sup>20</sup> The parallel dispersion of conduction and valence bands gives a structure in the band-to-band absorption (see Ref. 19 and inset of Fig. 2), and enhances also the excitonic effect. There exist several indications for the partly excitonic nature of the  $E_1$  transition: (i) the observed oscillator strength is much higher than calculated for band-to-band

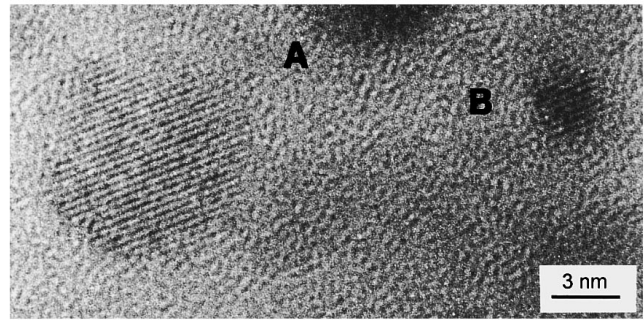


FIG. 1. High-resolution electron microscopy image of Ge nanocrystals, obtained with a Philips CM30 electron microscope, operating at 300 kV.

transitions;<sup>20</sup> (ii) calculations of  $\epsilon_2$  for diamond with excitonic effect<sup>21</sup> are in much better agreement with experiment; and (iii) the observed polarization-dependent stress-induced splitting of the  $E_1$ - $E_1 + \Delta_1$  transition in Ge and GaAs can be explained only by electron-hole exchange on the exciton.<sup>22</sup>

In a small quantum dot the  $\mathbf{k}$  vector is not a good quantum number anymore, and the selection rule related to the conservation of crystal momentum is broken by confinement. Thus optical transitions can occur that correspond to indirect transitions in the bulk,<sup>10,23</sup> so that the notion of transition between parallel bands in the  $\Gamma$ - $L$  direction becomes meaningless, and the peak in the absorption is expected to disappear. The reduction of the joint density of states, in turn, tends to wash out the excitonic effect, and to subtract further oscillator strength from the  $E_1$  transition. Thus it is reasonable that the  $E_1$  transition behaves differently from  $E_2$ , and that its total oscillator strength decreases in small Ge quantum dots. These arguments are in agreement with our experimental findings, as well as with the theoretical results for Si quantum dots:<sup>13</sup> both experiment (see Fig. 2) and the theory of Ref. 13 indicate, in fact, a transfer of oscillator strength from lower to higher energies.

The influence of the matrix on the optical response of the quantum dots is not expected to be relevant, on the basis of

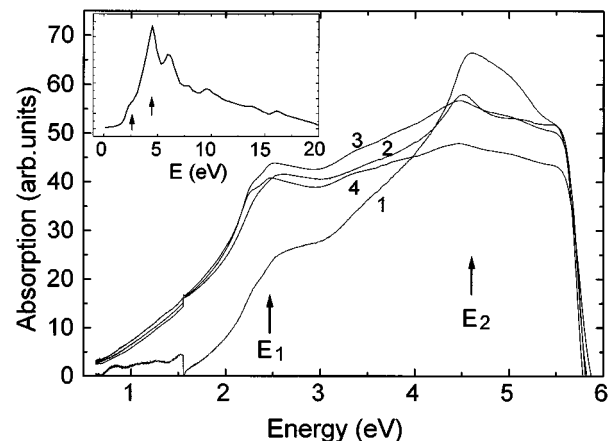


FIG. 2. Optical absorption of Ge nanoparticles. The difference between the absorption of samples containing the Ge nanoparticles and that of a reference sample without Ge is reported. The two main peaks are the  $E_1$  and  $E_2$  structures. The spectra are normalized to the Ge quantity (the jump at about 1.55 eV has an instrumental origin). Inset: calculated  $\mathbf{k} \cdot \mathbf{p}$  absorption spectrum for bulk Ge.

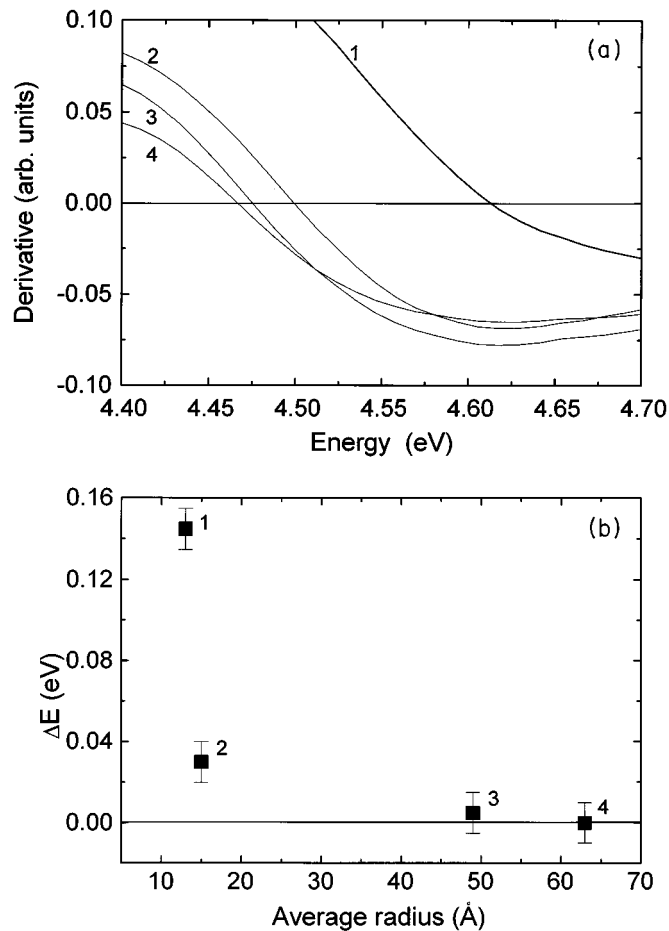


FIG. 3. (a) First derivative of the absorption spectra reported in Fig. 2, in the spectral region corresponding to the  $E_2$  peak. (b) Variation of the energy position of the  $E_2$  peak, corresponding to the zero crossing of the derivative, with respect to the bulk energy gap. (The position of the  $E_2$  peak, for the biggest nanoparticles agrees, at room temperature, with data reported in Ref. 24 for bulk Ge.)

the following considerations. Concerning possible effects of stress on the optical spectra, we underline that the room-temperature energy position of the peaks for the biggest particles is coincident within a few  $10^{-2}$  eV with the  $\epsilon_2$  data

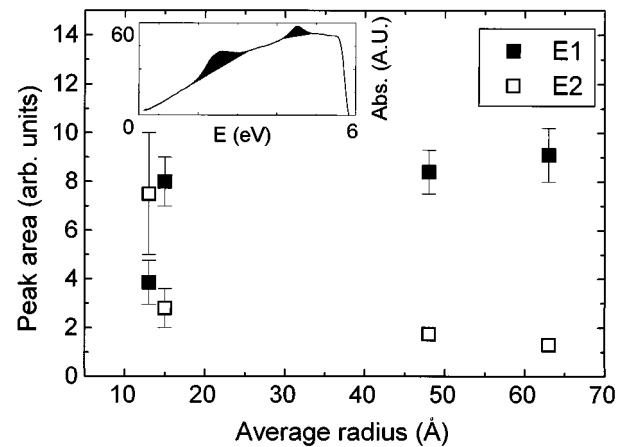


FIG. 4. Integrated oscillator strength of  $E_1$  and  $E_2$  structures obtained by subtracting the Ge background (as indicated in the inset for sample 2). Error bars are indicated when larger than point size.

obtained by Aspnes and Studna by ellipsometry<sup>24</sup> and that the general tendency of the spectral structures versus stress<sup>22</sup> is to shift without change of the oscillator strength; in addition, Ge does not wet the matrix (consequently the interaction is minimized) and the matrix itself is amorphous, so that the requirement of lattice matching is not as stringent as in the epitaxial growth.<sup>7,17</sup> Furthermore, it is worth noting that the good agreement between our results for the biggest particles and ellipsometry data for bulk samples<sup>24</sup> proves that dipole interactions between grains and matrix as well as other interface effects play a minor role; in any case, they could not explain the different behavior of  $E_1$  and  $E_2$ .

In conclusion, a comparative study of the  $E_1$  and  $E_2$  structures versus size has been carried out in Ge quantum dots, grown by means of a self-organization technique applied for the first time to semiconductors. The main results can be summarized as follows: (i) blueshift of  $E_2$  with size reduction; (ii) strong decrease of  $E_1$  with size reduction due to its partly excitonic nature; and (iii) evidence of oscillator strength transfer towards  $E_2$ , in agreement with the prediction of Wang and Zunger for Si quantum dots.

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<sup>18</sup>In the calculation, one must take into account the exponential decay of the light intensity in the absorptive Ge encased in the matrix, as well as the multiple internal reflections. It has been

checked that both effects determine relatively small variations, which never exceeded a few percent in our samples.

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